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Analysis of Volatile Hazardous Substances by GC/MS

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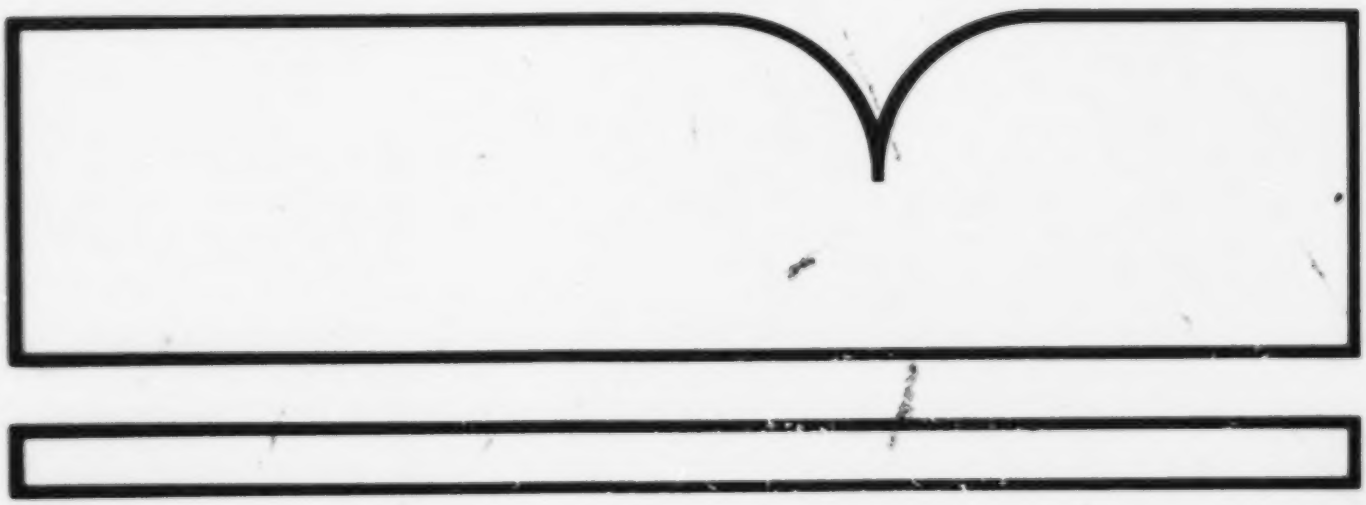

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16. ABSTRACT

The United States Environmental Protection Agency (EPA) has proposed methods for analysis of volatile organic priority pollutants by gas chromatography/mass spectrometry (GC/MS) using purge-and-trap techniques. We have evaluated 15 additional compounds which appear on the Hazardous Substance List and determined that these volatile organics are suitable for analysis by the proposed methods. For most of the compounds evaluated, detection limits are less than 10 ppb. Recovery and precision measurements demonstrate that the method provides semiquantitative analysis for these volatile hazardous substances.

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Analysis of Volatile Hazardous Substances by GC/MS

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Abstract

The USEPA has proposed methods for analysis of volatile priority pollutants by gas chromatography/mass spectroscopy (GC/MS) using purge-and-trap techniques. Fifteen additional compounds, which appear on the Hazardous Substance list, were evaluated; these volatile organics were determined suitable for analysis by the proposed methods. For most of the compounds evaluated, detection limits were less than 10 ppb. Recovery and precision measurements demonstrate that the method provides semiquantitative analysis for these volatile hazardous substances.

Introduction

In 1979, the United States Environmental Protection Agency (USEPA) proposed methods for analysis of a wide variety of "priority pollutants," substances which were selected on the basis of their toxicity and their frequency in the environment (1). The EPA subsequently published a list of "hazardous substances" that must be monitored by dischargers whenever the substances are expected to be present (2). This list contains 79 additional compounds and metals for which the EPA has not proposed methods of analysis. Many of these compounds are volatile organics; of these, 11 are amines and are being studied separately. A few others were eliminated for technical reasons (*i.e.*, reactivity with water). This paper presents data indicating that many of the volatile organic chemicals on the hazardous substance list can be analyzed by EPA's proposed Method 624 (3).

The EPA had divided the priority pollutants into 16 groups based on acceptable methods of analysis. These primarily require GC with various detectors, including MS. Volatile organics are analyzed by purge-and-trap techniques (4), wherein compounds are purged from the aqueous solution by bubbling with an inert gas into a trap containing Tenax sorbent and silica gel. The sample is swept from the trap into a gas chromatograph by rapid heating. The analytes then are separated by GC and detected with either specific ionization detection or MS. In this study, selective ion monitoring was used to quantitate all peaks.

Experimental

EPA Method 624 requires GC/MS analysis of certain volatile organics in aqueous systems. A Valco total organics concentrator was used as the purge-trap device and was set for the following parameters: purge time, 12 min; desorption time, 4 min; desorption temperature, 180°C; bakeout time, 7 min; bakeout temperature, 180°C; valve temperature, 190°C; and nitrogen flow, 40 ml/min. The 25-cm trap contained 0.5-cm glass wool, 1-cm 3% OV-1, 15-cm Tenax-GC (60-80 mesh), 8-cm Davison type-15 silica gel (Applied Science; 35/60 mesh), followed by 0.5-cm glass wool, respectively, from inlet to outlet. The Finnigan 3200 GC/MS utilized a 2-m × 2-mm i.d. glass column containing 1% SP-1000 on Carbopack B (Supelco; 60/80 mesh). A Finnigan Incos data system was used to collect and process the data.

Each compound was studied first by direct injection to confirm mass spectral similarity to the National Bureau of Standards reference library. The major ion plus two characteristic ions were evaluated by obtaining a calibration curve over the range of 5 to 2000 ng injected with multiple ion monitoring. Quantitation was based on external standards.

Secondary effluent was obtained from Los Coyotes, a publicly owned treatment works (Cerritos, California). Seven replicate 5-ml samples of secondary effluent were spiked with the same mixture and analyzed for precision of data. In addition, a second mixture was prepared to obtain spike levels up to 10 times those of the first mixture. Seven replicates of this mixture in secondary effluent were also analyzed.

Results and Discussion

All compounds exhibited mass spectra identical to those in the National Bureau of Standards reference library. In general,

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the base peak was selected as the ion for quantitation; however, in some cases of coeluting or only partially resolved peaks, the base peak could not be used. In these instances, a secondary unique mass was selected so that no interferences would exist from neighboring peaks. Table I shows the selected ions and their relative abundances.

Detection limits were measured by direct injection and purge from distilled water (Table II). Minimum detectable amount was defined as the amount of material required to obtain an area of 1000 counts under the selected ion chromatogram for a given compound. The efficiency of the purge-and-trap device, compared to direct injection, was also calculated and listed (Table II). Purge efficiency is calculated as the recovery from purging divided by the recovery from direct injection. Those compounds having high water solubility (*i.e.*, alcohols and aldehydes) had the lowest purge efficiency and therefore had the highest detection limits in water. Preliminary data showed that formaldehyde could also be analyzed by this technique, but the method specifies monitoring a mass range, which excludes the masses for formaldehyde of 29 and 30 amu.

The analysis was performed by both internal standard and external calibration techniques. It was found that the precision of the internal standard was about 10% relative standard deviation (% RSD). Due to independent variation of the analytes, causing substantial error in measurement, external calibration was used.

To determine measurement precision, 5 to 7 replicate spikes of a mixture of all compounds were placed in 5-ml aliquots of secondary effluent taken from the wastewater treatment works. These were analyzed by the purge-and-trap method, and Figure 1 shows a typical chromatogram of the compounds purged from secondary effluent. Most of the peaks were clearly separated from their neighbors, except for benzonitrile and benzyl chloride, which coelute. This pair, however, were easily separable by their unique mass peaks, and the results are shown in Table III. These spike levels were at 10 to 20 times the detection limit; the precision was poor, averaging 18% relative standard deviation. However, when precision studies were repeated at spike levels up to 10 times higher, precision increased to an average of 8% relative standard deviation.

The above results indicate that EPA Method 624 can be expanded to include 15 volatile organics currently listed as hazardous substances. The method provides semi-quantitative results for these compounds with precision similar to that for priority pollutants.

Table I. Selected Ions and Relative Abundances

	Retention Time	Quantitation Ion (m/e)	Abundance (%)
Acetaldehyde	2:19	43	100
Allyl alcohol	9:21	57	100
Allyl chloride	8:44	41	100
Amyl acetate	24:54	70	29
Benzonitrile	27:11	103	100
Benzyl chloride	27:17	91	100
n-Butyl acetate	21:57	56	33
Carbon disulfide	7:39	76	100
Crotonaldehyde	14:22	70	88
Cyclohexane	13:10	56	100
1,2-Dibromoethane	17:15	107	100
Furfural	20:03	96	78
Isoprene	12:49	67	100
Methyl methacrylate	18:39	41	100
Vinyl acetate	13:23	43	100
2-Bromo-1-chloropropane (surrogate standard)	17:34	77	100

Table II. Detection Limits (ug/L) and Purge Efficiency

	Direct Injection	Distilled Water Purge	Purge Efficiency (%)
Acetaldehyde	80	200	45
Allyl alcohol	3	200	2
Allyl chloride	2	2	88
Amyl acetate	1	2	69
Benzonitrile	1	10	5
Benzyl chloride	2	6	43
n-Butyl Acetate	2	3	64
Carbon Disulfide	1	1	120
Crotonaldehyde	5	50	8
Cyclohexane	1	2	66
1,2-Dibromoethane	1	1	74
Furfural	2	100	1
Isoprene	3	3	82
Methyl methacrylate	2	3	69
Vinyl acetate	1	1	78
2-Bromo-1-chloropropane (surrogate standard)	1	1	83

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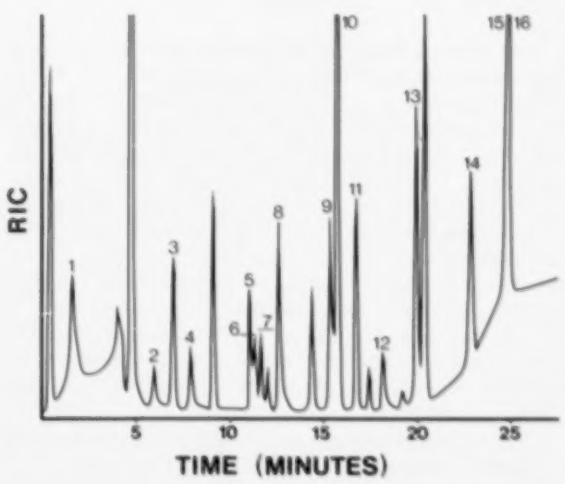

Figure 1. Reconstructed ion chromatogram for purge-and-trap analysis of volatile hazardous substances. Chromatographic and spectrometric conditions are given in the text. Numbered peaks are: 1) acetaldehyde, 2) carbon disulfide, 3) allyl chloride, 4) allyl alcohol, 5) isoprene, 6) cyclohexane, 7) vinyl acetate, 8) crotonaldehyde, 9) 1,2-dibromoethane, 10) 2-bromo-1-chloropropane, 11) methyl methacrylate, 12) furfural, 13) *n*-butyl acetate, 14) amyl acetate, 15) benzonitrile, and 16) benzyl chloride.

Table III. Spike Levels of Purged Compounds

	Spike (ppb)	% Recovery*	% RSD**	Spike (ppb)	% Recovery*	% RSD**
Acetaldehyde	1,400	74	18	7,000	110	13
Allyl alcohol	3,930	120	17	9,820	98	7
Allyl chloride	68	83	12	170	96	8
Amyl acetate	36	120	13	360	110	7
Benzonitrile	408	120	19	816	110	23
Benzyl chloride	94	82	28	944	100	7
n-Butyl Acetate	83	100	18	208	110	3
Carbon Disulfide	39	95	15	39	25	12
Crotonaldehyde	940	110	28	4,700	120	4
Cyclohexane	36	88	18	72	100	6
1,2-Dibromoethane	48	96	14	240	110	4
Furfural	1,270	120	34	12,700	96	10
Isoprene	98	88	12	246	100	4
Methyl methacrylate	73	110	16	182	110	4
Vinyl acetate	72	96	15	72	110	2
2-Bromo-1-chloropropane (surrogate standard)	20	92	11	160	98	11

*Recovery from secondary effluent relative to distilled water
**Relative standard deviation of 5 to 7 replicates

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